Physical Properties of Hydrocarbons

PART 20–Halogenated Methanes

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As a collective group, fluorocarbon production was about 500 million pounds in 1966. The properties that made the fluorocarbons valuable are their high density, low viscosity, low surface tension, good stability, and low toxicity. The original use for fluorocarbons—refrigerants—still accounts for 30 percent of the usage and continues to grow steadily. Fluorocarbon-11 and Fluorocarbon-12 are the most commonly used refrigerants. The phenomenal growth of aerosol containers boosted the fluorocarbons into a big volume business. Currently, aerosols take almost 50 percent of the fluorocarbon production, but this market will probably drop off some as new nonfluorocarbon propellants invade the field. As in refrigerants, Fluorocarbon-11 and Fluorocarbon-12 dominate the aerosol field. The loss of business in aerosols will be more than offset by rapid growth in fluorocarbon usage as degassers, blowing agents for rigid urethane foam (mainly Fluorocarbon-11), and plastics.

The field is dominated by Du Pont with 50 percent of the market followed by Allied Chemical with 25 percent of the market. Typically, the products are produced by reacting hydrogen fluoride with carbon tetrachloride, chloroform, or perchloroethylene.

Because of their extensive use in aerosols and refrigeration, Fluorocarbon-11 and Fluorocarbon-12 have been extensively studied and their physical properties are available over a wide temperature range. Considerably less data are available on Fluorocarbon-13 and Fluorocarbon-14.

Vapor Pressure and Critical Properties. The critical properties and the vapor pressures up to the critical point are available from the literature for all four compounds.[1,2,3]

Heat of Vaporization. The heat of vaporization has been determined for Fluorocarbon-13 up to its critical temperature.[2] Data on Fluorocarbon-11 and Fluorocarbon-12 have been compiled from −100° C to +70° C.[2] For Fluorocarbon-14, the heat of vaporization is available only at the boiling point.[1] The data for Fluorocarbon-11, -12, and -14 have been extended by the Kharbanda nomograph of the Watson equation.[4] Calculated values gave average and maximum errors of 1.8 percent and 3.5 percent, respectively, when compared to 7 experimental values.

Heat Capacity. A number of investigators have determined the vapor heat capacities of the Fluorocarbon compounds.[5,6,7] The experimental results of all investigators agree within 1 percent of each other.

The liquid heat capacities of Fluorocarbon-11 are available from −93° C to +75° C.[8,9] Data on Fluorocarbon-12 cover the range of −80° C to +20° C.[10,11] The Du Pont bulletin[1] presents the heat capacity for Fluorocarbon-13 at −30° C and for Fluorocarbon-14 at −80° C. These data were extended over a wider temperature range by the equation: liquid heat capacity equals a constant divided by the liquid density. The constant was calculated for each compound from an experimental point. The author found that this estimation method gave much better results than other methods. When compared with 8 experimental values from Fluorocarbon-11 and -12, the error averaged 1.8 percent with a maximum error of 7.7 percent. The liquid heat capacities of halogenated compounds are lower than most compounds, and do not increase as rapidly with temperature. Because of this, estimation methods generally give high results, especially with increasing temperature.

Liquid Density. The liquid density has been experimentally determined up to the critical point for Fluorocarbon-11[2,3] and Fluorocarbon-13.[2,12] Fluorocarbon-12 data are available up to 60° C.[2] Only the density at −80° C has been measured for Fluorocarbon-14.[1] The data have been extended to the critical point by the method of Lydersen and coworkers.[13] This method, which relates the change in density to the critical compressibility and reduced temperature, gave an average error of 0.6 percent when compared with 15 experimental values of Fluorocarbon-11 and -12.

Viscosity. Witzel and Johnson[14] have measured the vapor viscosity of all four compounds from −40° C to +150° C. This information has been supplemented by other literature data,[15,16,17] and extended over the −100° to +400° C range by the estimation method of Bromley

TABLE 20-1—Physical Properties of Halogenated Methanes

Compound	Commercial Product Code	Boiling Point °C	Freezing Point °C	Molecular Weight	CRITICAL PROPERTIES °C t_c	PSIA P_c	g/ml d_c
trichlorofluoromethane	Fluorocarbon—11	23.8	−111	137.4	198.0	635	0.554
dichlorodifluoromethane	Fluorocarbon—12	−29.8	−158	120.9	112.0	597	0.558
chlorotrifluoromethane	Fluorocarbon—13	−81.4	−181	104.5	28.9	561	0.578
tetrafluoromethane	Fluorocarbon—14	−128.0	−184	88.0	−45.7	543	0.626

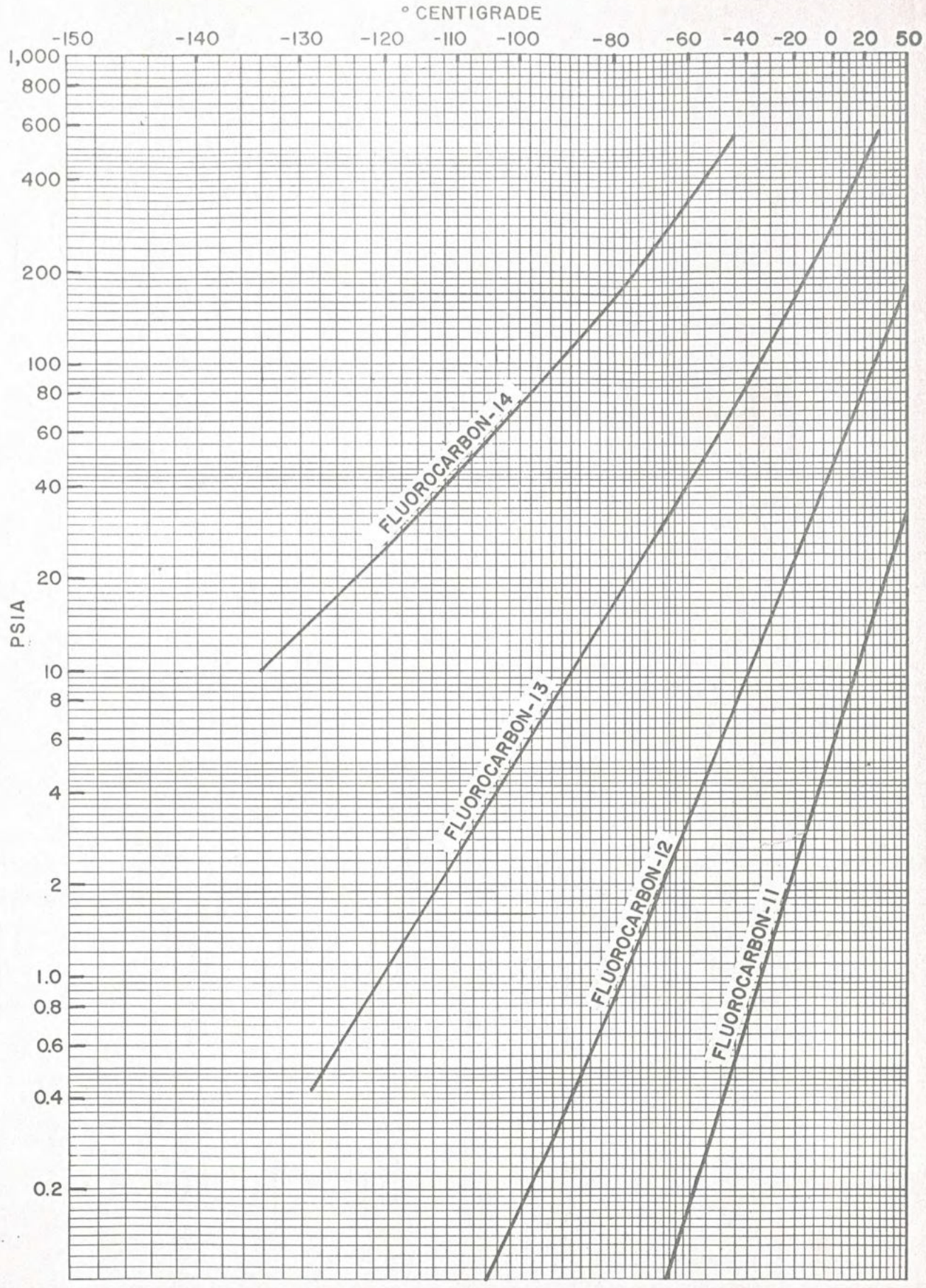

Fig. 20-1—Gives the vapor pressure of halogenated methanes from — 130° C to + 50° C.

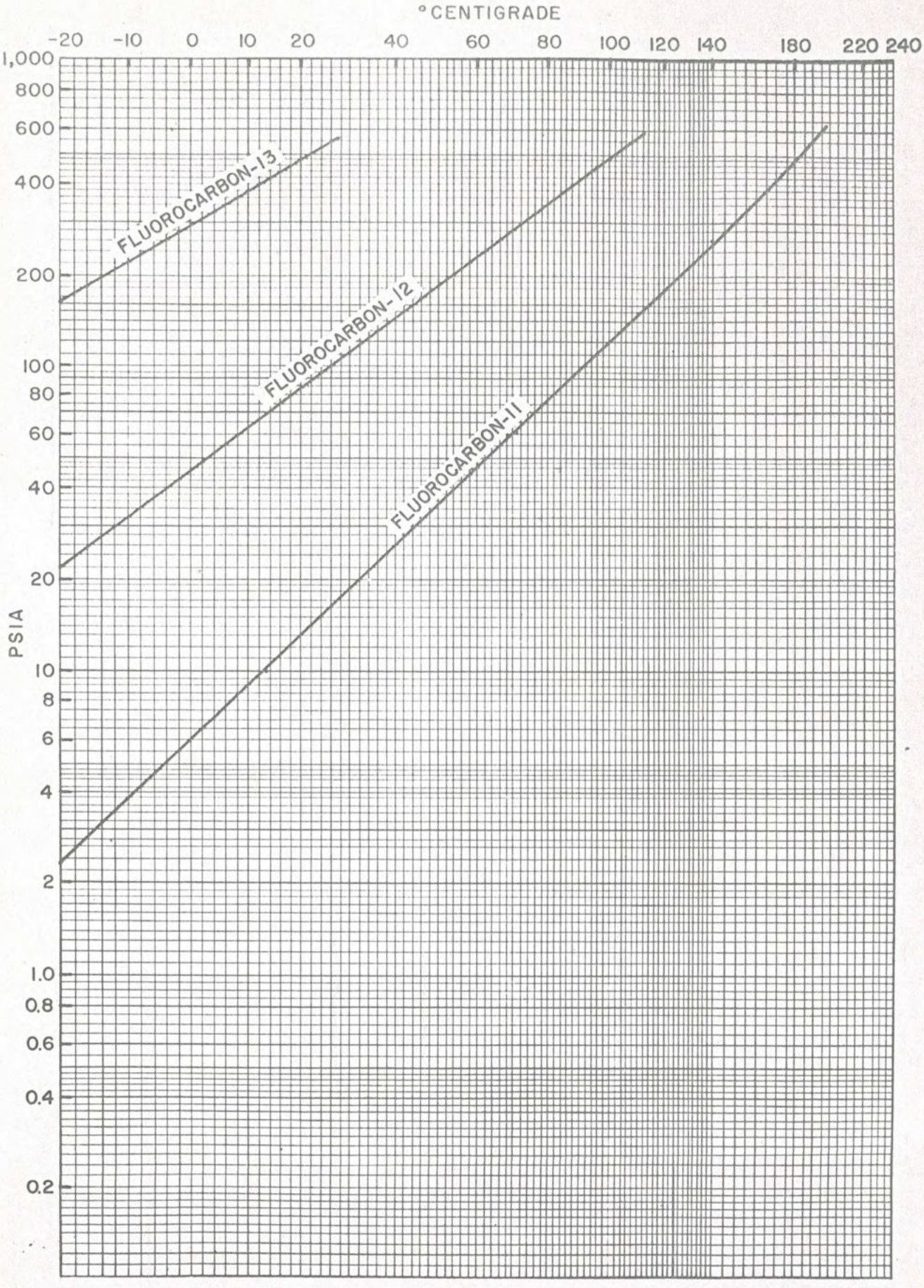

Fig. 20-2—Gives the vapor pressure of halogenated methanes from — 20° C to + 200° C.

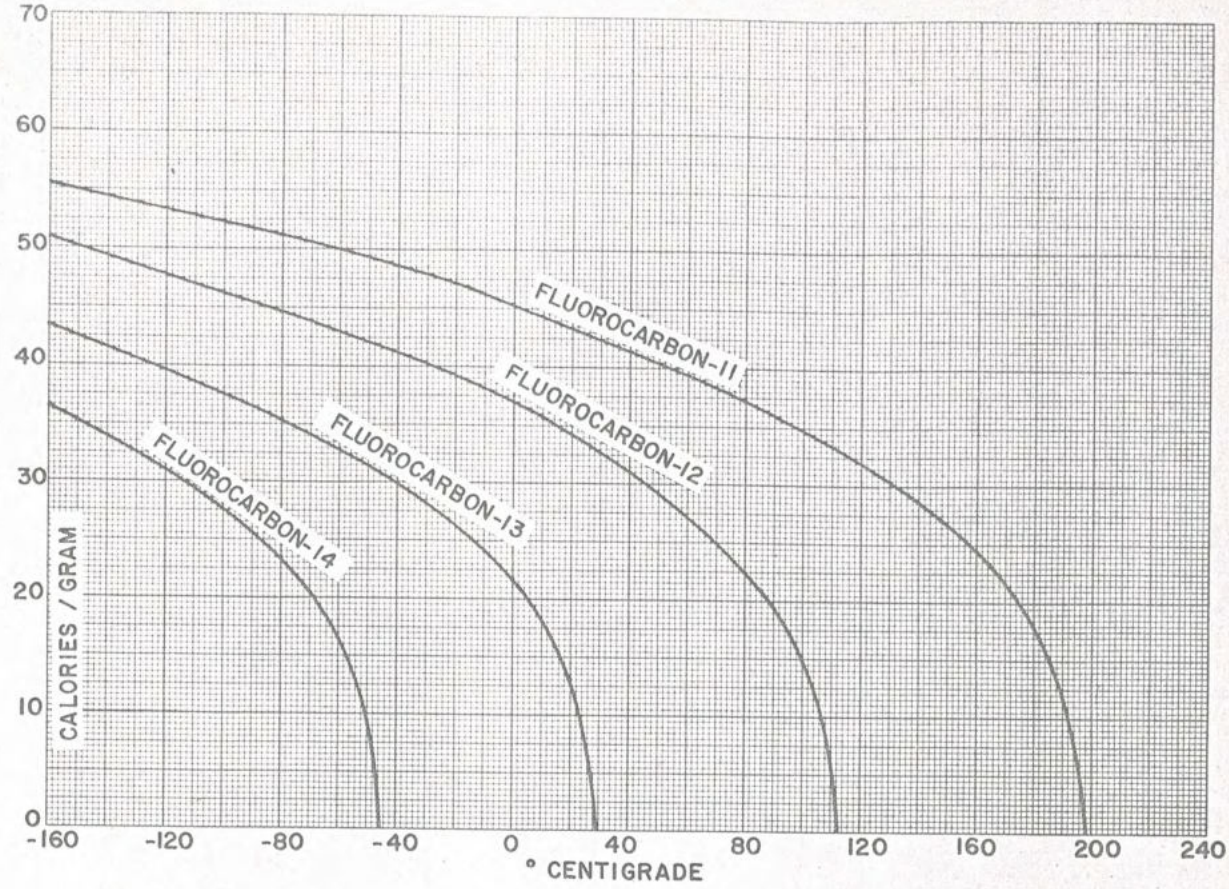

Fig. 20-3—Gives the heat of vaporization of halogenated methanes from — 160° C to + 200° C.

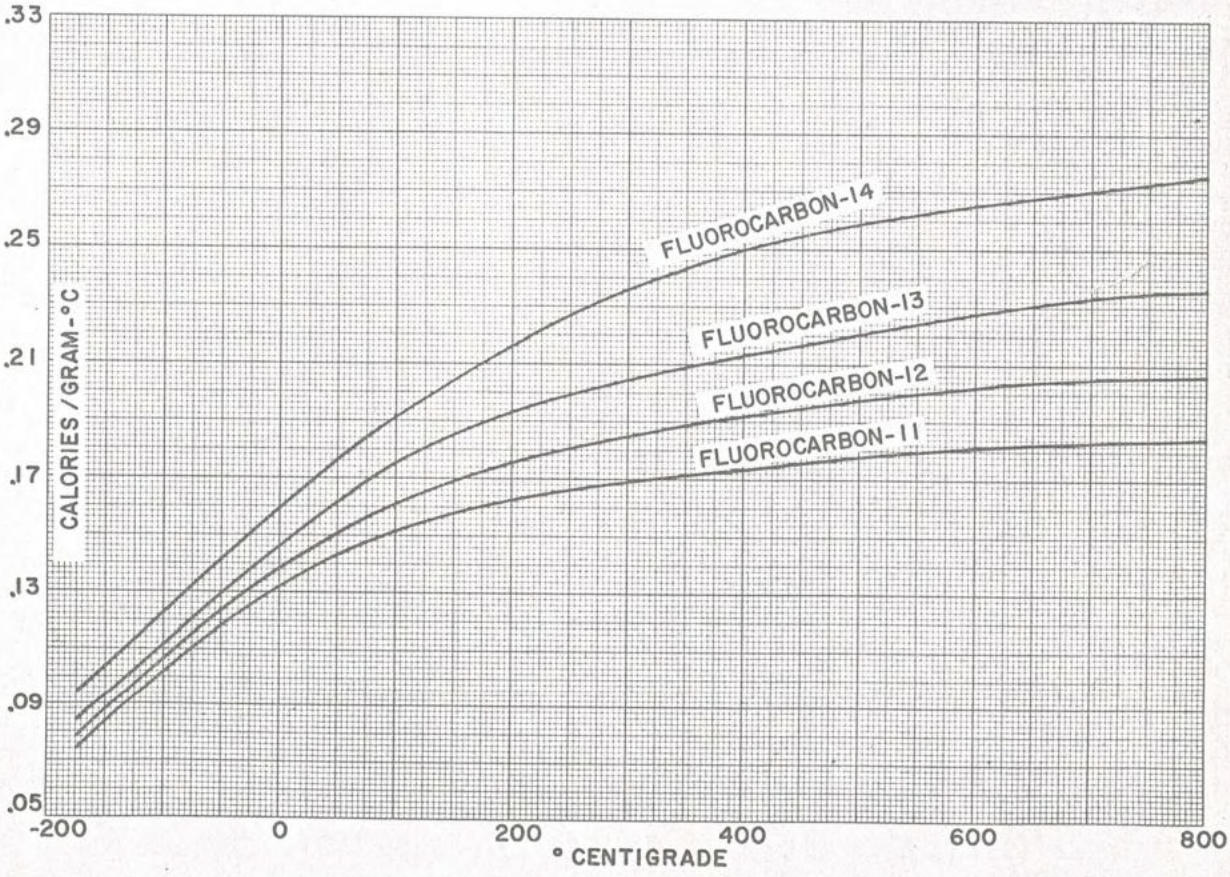

Fig. 20-4—Gives the vapor heat capacity of halogenated methanes from — 175° C to + 800° C.

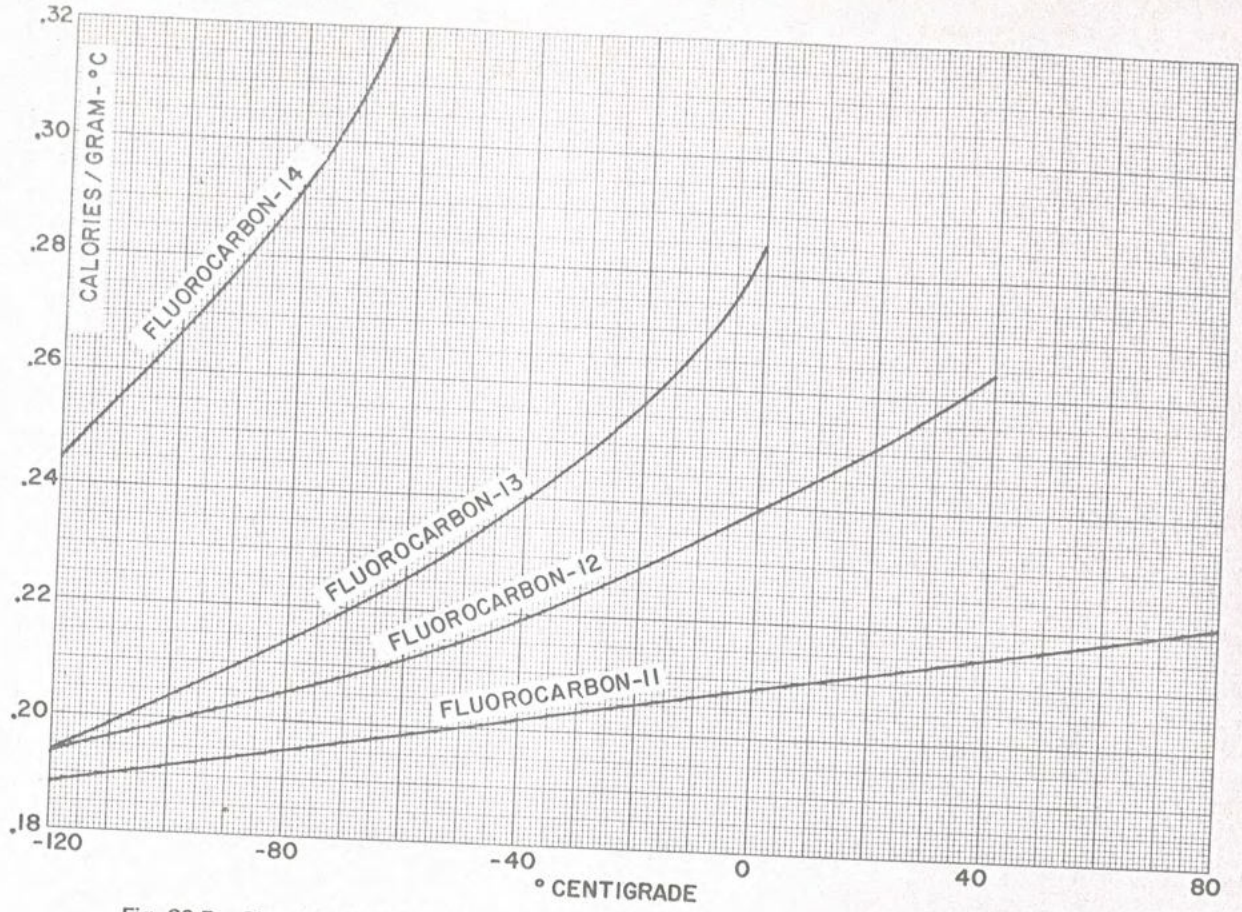

Fig. 20-5—Gives the liquid heat capacity of halogenated methanes from — 120° to + 80° C.

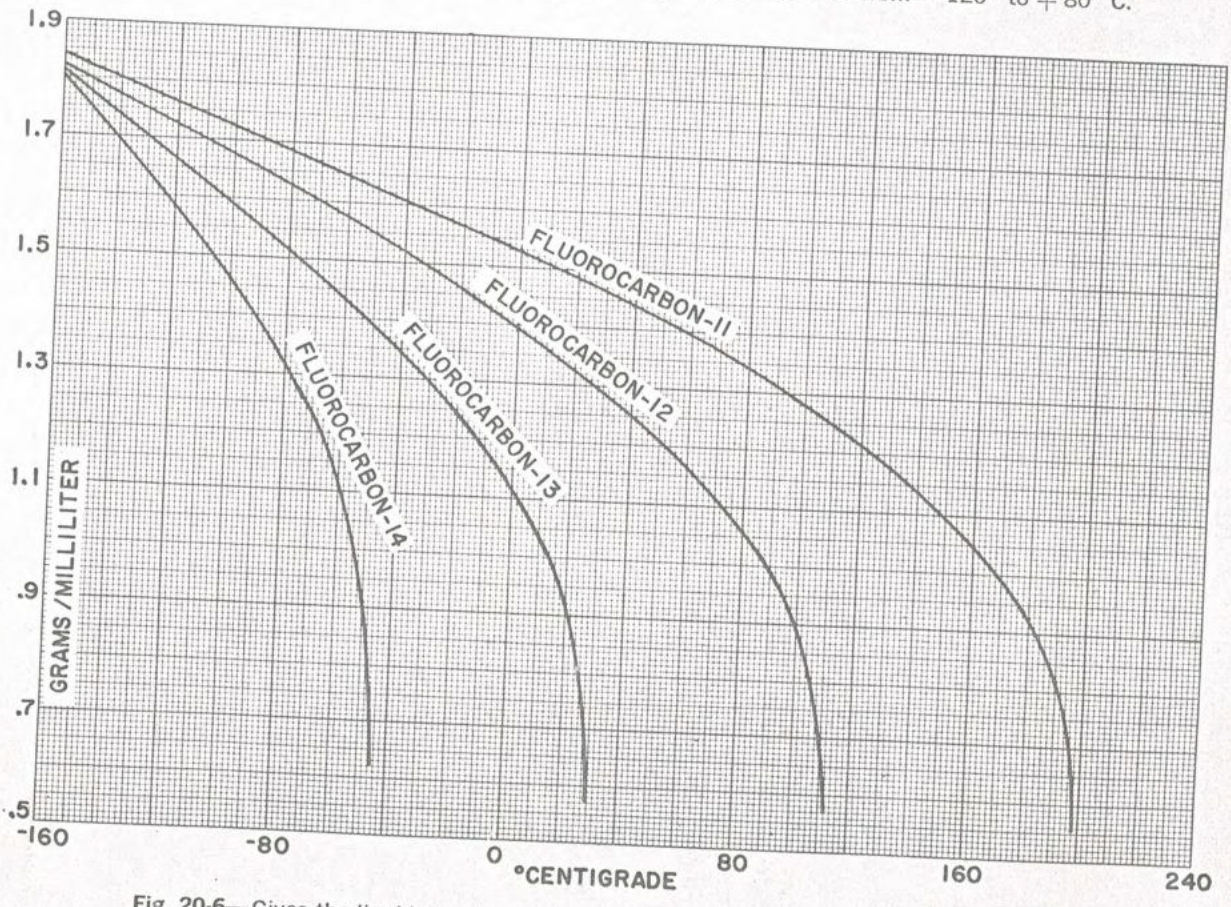

Fig. 20-6—Gives the liquid density of halogenated methanes from — 160° C to + 200° C.

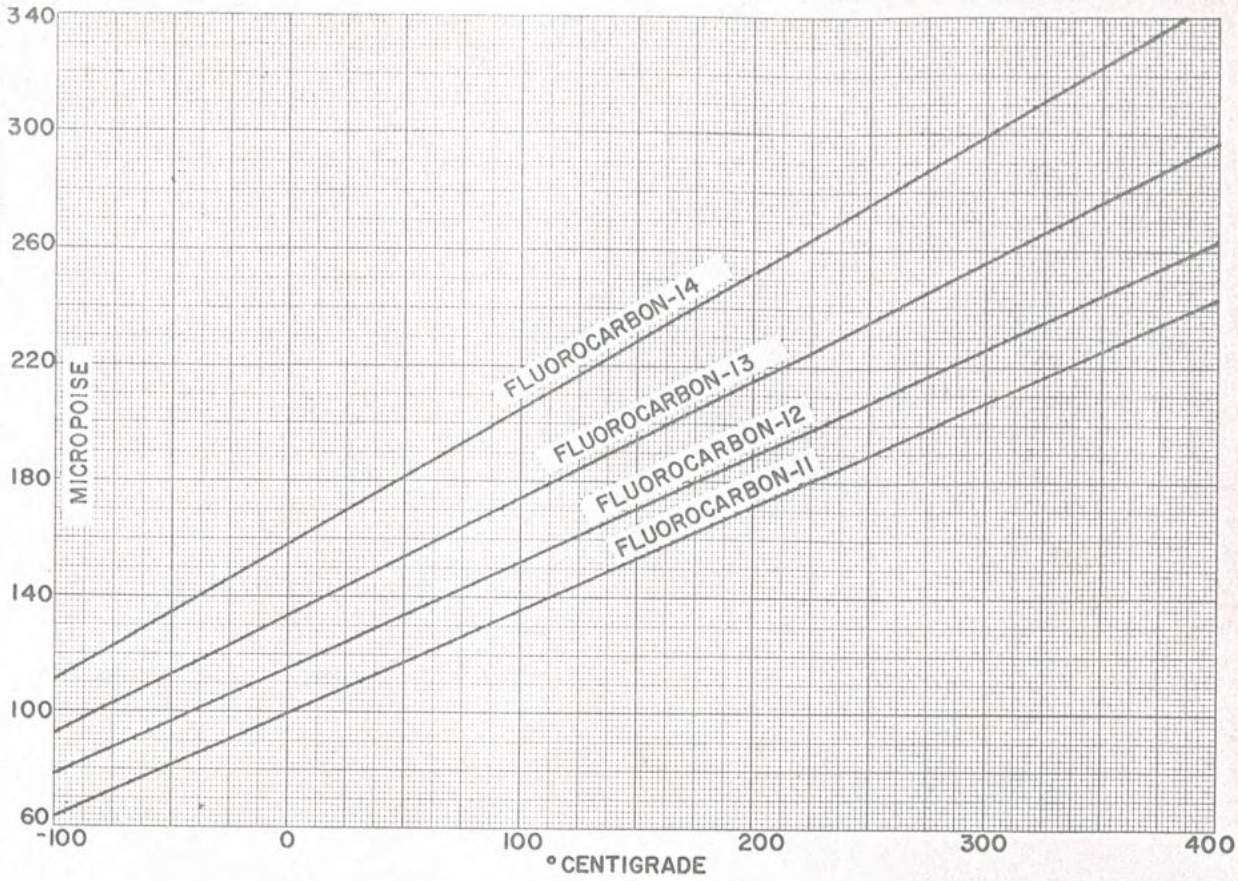

Fig. 20-7—Gives the vapor viscosity of halogenated methanes from — 100° C to + 400° C.

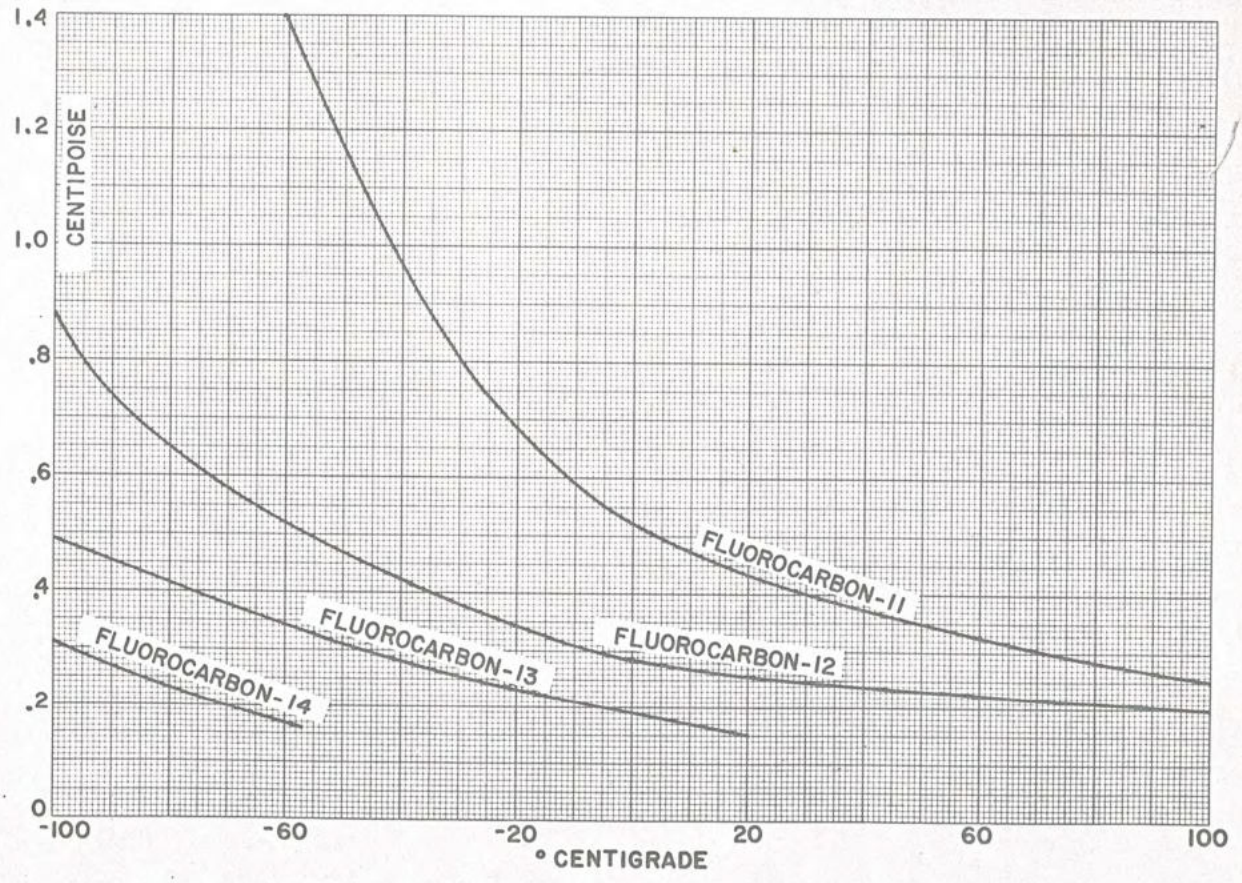

Fig. 20-8—Gives the liquid viscosity of halogenated methanes from — 100° C to + 100° C.

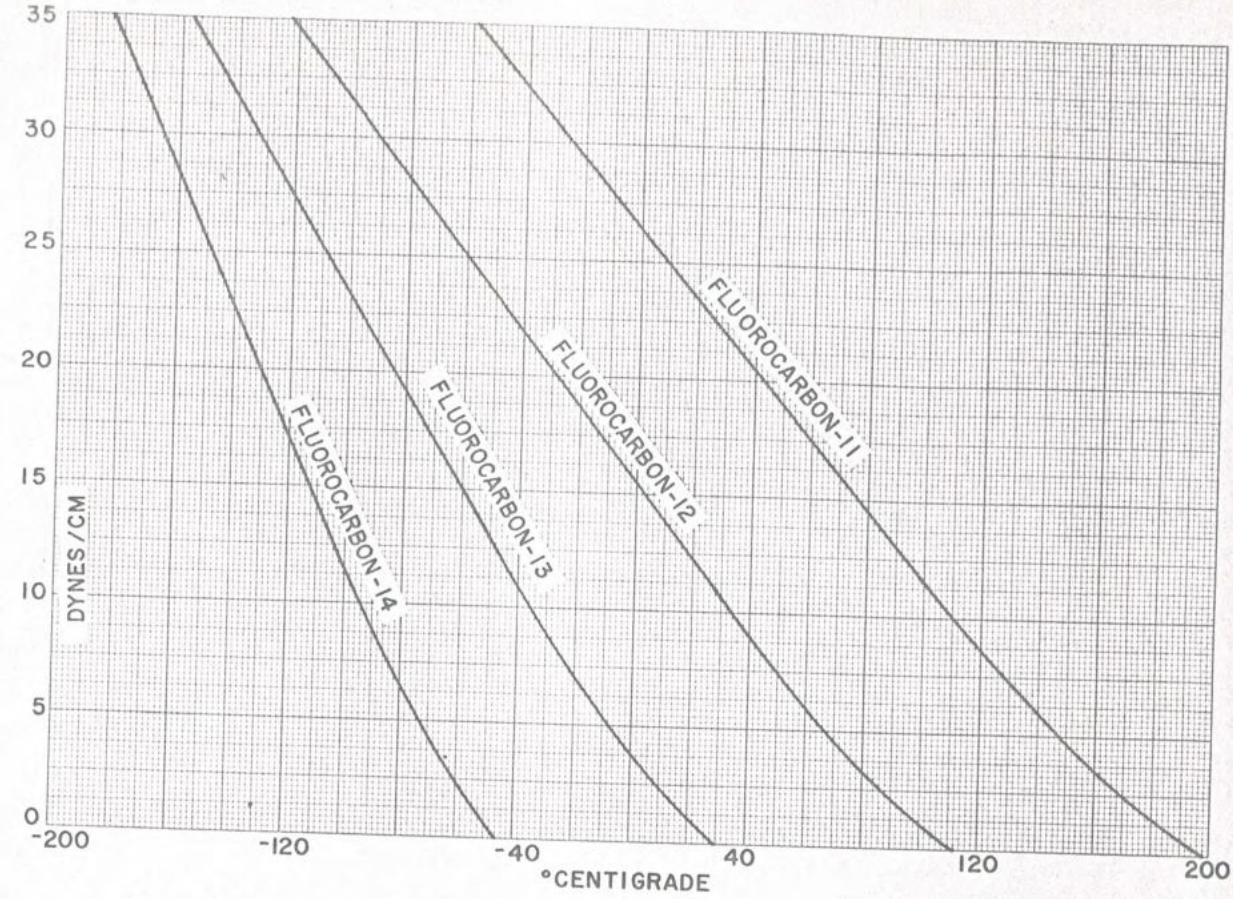

Fig. 20-9—Gives the surface tension of halogenated methanes from — 180° C to + 200° C.

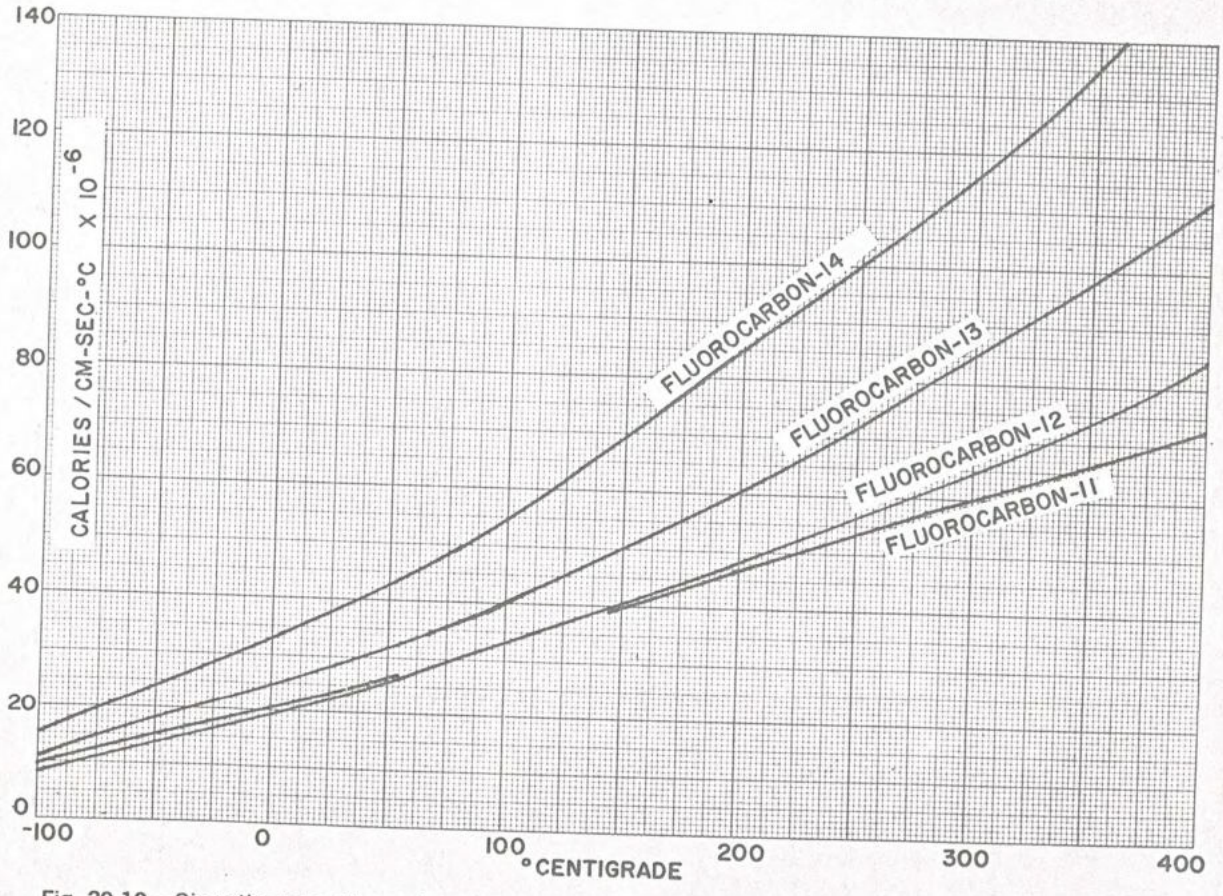

Fig. 20-10—Gives the vapor thermal conductivity of halogenated methanes from — 100 ° C to + 400 ° C.

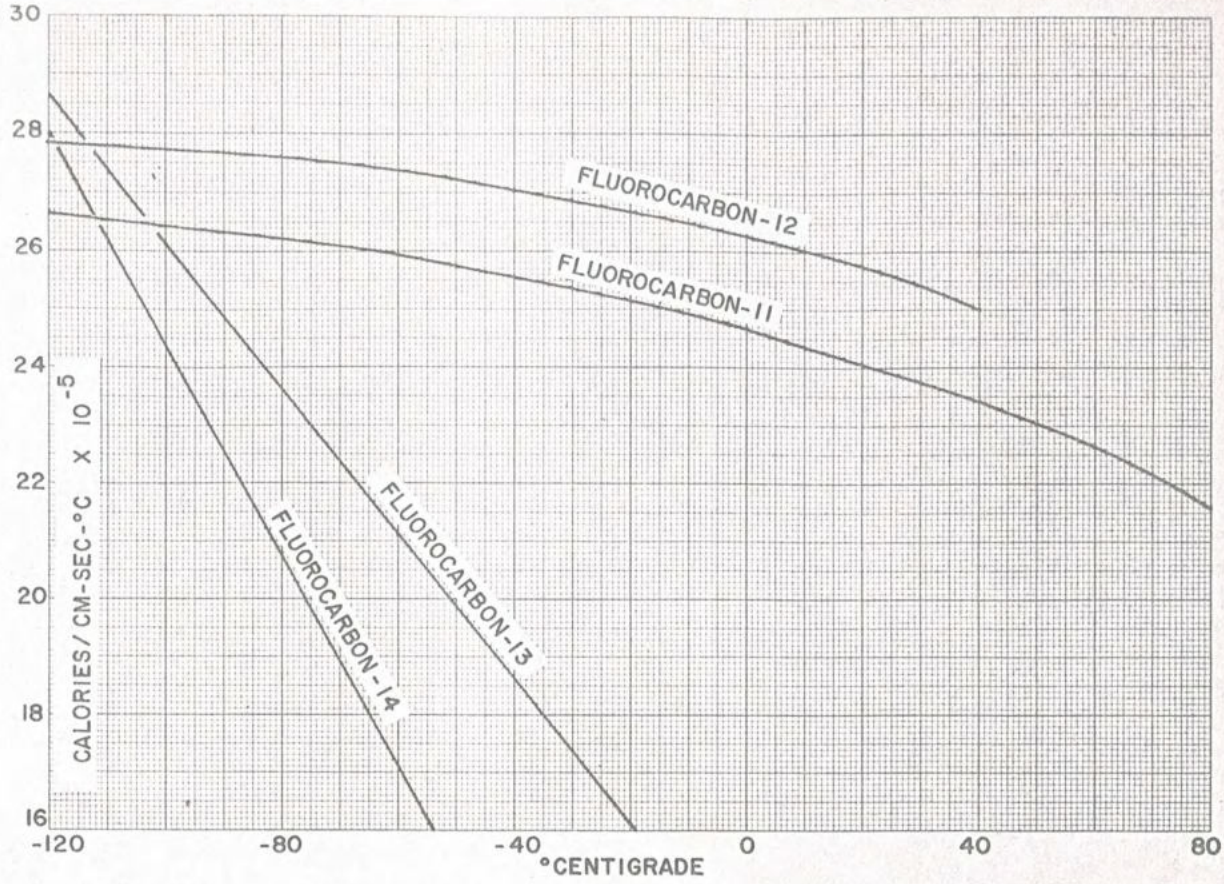

Fig. 20-11—Gives the liquid thermal conductivity of halogenated methanes from — 120° C to +80° C.

and Wilke.[18] The author used a different constant than recommended by Bromley and Wilke because the vapor viscosity of fluorocarbons is lower than estimation methods indicate. Using a lower constant, the author obtained an average error of 3 percent for 16 experimental points.

Liquid viscosities have been determined for Fluorocarbon-11 and Fluorocarbon-12 up to 100° C.[2,14] For the other two fluorocarbons, it has been necessary to estimate the viscosity over the entire temperature range. There is no highly accurate estimation method for fluorocarbons. Some methods give values much higher than the actual values; other methods give very low results. Errors of 50 to 100 percent are common. The author modified the method of Thomas,[13] which typically gives low results, and obtained average and maximum errors of 17 percent and 60 percent, respectively, for 8 experimental values on Fluorocarbon-11 and Fluorocarbon-12.

Surface Tension. Surface tensions are available only at one temperature for all four compounds.[1] The nomograph of Kharbanda[19] has been used to extend the data over a wide temperature range.

Thermal Conductivity. The vapor thermal conductivities have been calculated by the method of Owens and Thodos,[20] which relates thermal conductivity to a pseudo-critical thermal conductivity and the reduced temperature. The pseudo-critical constant was determined from available experimental thermal conductivities.[1,16,21]

With no reliable data available on the liquid thermal conductivities, the estimation method of Robbins and Kingrea[22] has been used. The error is probably ±10 percent.

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Indexing Terms: Carbon Tetrafluoride-9, Chlorinated Hydrocarbons-9, Chlorotrifluoromethane-9, Computations-4, Dichlorodifluoromethane-9, Fluorinated Hydrocarbons-9, Heat-7, Halogenated Hydrocarbons-9, Liquid Phase-5, Physical Properties-7, Pressure-6, Properties/Characteristics/-7, Temperature-6, Tetrafluoromethane-9, Trichlorofluoromethane-9, Vapor Phase-5.

Part 21 "Fluorinated Hydrocarbons" will appear in an early issue.